Natural Gas Conversion VIII
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DIRECT SYNTHESIS OF PROPANE/BUTANE FROM SYNTHESIS GAS

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Abstract

Efficient conversion of syngas into LPG over a hybrid catalyst is a novel method for the synthesis of clean fuel from natural gas, coal or biomass. Hybrid catalysts based on methanol synthesis catalyst and zeolite were investigated in a fixed bed reactor. Experimental results demonstrated that the modified Cr-Zn methanol catalyst and β-zolite increased the activity, selectivity and stability of hybrid catalyst. The newly developed catalyst showed one through CO conversion of 81% and selectivity of 78% and 15% for LPG and naphtha, respectively at 370 ^{o}C and 5.1 MPa. Bench plant is now under operation.

1. Introduction

Syngas (H_2/CO) production from natural gas or coal is the established technology. The LPG synthesis from syngas would be most promising but remain unexploited technology. Fig. 1 shows relationship between above technologies.

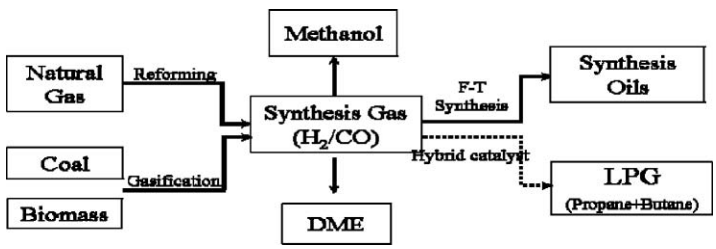

Fig. 1 Three Routes for LPG

The syngas, which is commercially produced by reforming of natural gas or gasification of coal or biomass, can be converted into hydrocarbons (LPG)

through methanol or DME as an intermediate in above processes.
As we have reported [1-4], LPG was directly synthesized from syngas over a hybrid catalyst which composed of methanol synthesis catalyst and zeolite. The hybrid catalyst that composed of Cu-Zn methanol synthesis catalyst and Y-type zeolite showed a good initial activity and selectivity for synthesis of LPG. However, its stability remained to be improved because the Cu-Zn catalyst deactivated under an atmosphere of CO_2 and water at high temperature. The hybrid catalyst consisted of Pd-based and β-zeolite showed a higher stability and activity than Cu-based catalyst. High catalyst cost is caused by high content of Pd in methanol catalyst would be obstructive to commercial application of this new process.
In this work, the performance of hybrid catalyst based on the modified Cr-Zn and β-zeolite by palladium was investigated, and a highly stable and active hybrid catalyst for directly synthesis of LPG from syngas was presented.

2. Results and discussion

2.1. The performance of hybrid catalysts for synthesis gas to LPG

Differently from F-T synthesis reaction mechanism[5-7], LPG was directly synthesized from syngas through methanol or DME as an intermediate over a hybrid catalyst. The hybrid catalyst exhibits two functions: methanol synthesis and selective conversion of methanol into hydrocarbons. Because of the synergistic effect of methanol synthesis catalyst and zeolite, the coexistence of both steps, methanol synthesis and methanol conversion in the single reactor, remove the limitation of thermodynamic equilibrium of methanol formation from syngas and CO conversion reaches high level (almost 100%) at low reaction pressure.
Usually the reaction temperature of conversion of methanol or DME into hydrocarbon was higher than 300^{o}C, and at that high temperature Cu-Zn methanol synthesis catalyst suffer from the deactivation with time on stream. Supported palladium catalyst for methanol synthesis on the other hand show higher stability but lower activity than Cu-Zn methanol catalyst, and addition of calcium into supported palladium promoted its activity.
Chromium and zinc oxide as methanol catalyst requires high temperature and pressure because of low activity for methanol synthesis. But it is more stable than the catalyst based Cu-Zn oxides at high temperature and high partial pressure of CO_2 and H_2O[8,9].
The hybrid catalyst employed is a mixture of Cr-Zn methanol synthesis catalyst and β-zeolites with a ratio of silica to alumina between 37 and 400.
Zeolite containing of Pd, was prepared by ion exchange method.
A pressurized flow type reaction apparatus with a fixed bed tubular reactor with an inner diameter of 6mm was used for this study. Details of the reaction

procedures and the product analysis have been described elsewhere.
Table 1 shows the promotion of LPG synthesis by the modification with small amount of palladium into Cr-Zn oxide. As Table 1 shows, Pd-free catalyst showed a low activity, because Cr-Zn had low activity for methanol synthesis at 2.1MPa. Added palladium in Cr-Zn resulted in the high activity for LPG synthesis, while keeping the LPG selectivity ((C_3+C_4) % in hydrocarbons) almost constant. That demonstrated that the small amount of Pd on Cr-Zn and β-zeolite benefited the activity and selectivity of hybrid catalyst for synthesis of hydrocarbons.

Table 1: The performance of hybrid catalysts as a function of palladium content in Pd/Cr-Zn

Catalyst	A	B	C	C	D
Reaction pressure (MPa)	2.1	2.1	2.1	5.1	5.1
CO Conversion (%)	21.4	23.9	33.9	66.8	72.0
Product Yield (C%)					
Hydrocarbons	12.5	12.6	20.6	40.3	46.8
DME	0.6	0.0	0.0	0.03	0.11
CO_2	8.9	11.2	13.3	26.5	25.1
Hydrocarbon Distribution (C%)					
C_1	5.0	3.9	3.8	6.4	2.3
C_2	11.5	10.0	8.9	8.0	3.0
C_3	45.1	45.2	48.2	47.4	37.4
C_4	31.2	33.9	31.9	31.3	40.6
C_5	5.4	5.5	5.4	5.2	9.7
C_{6+}	1.8	1.5	1.6	1.7	6.0
LPG(C_3+C_4)	76.3	79.1	80.2	78.7	78.0

Note: W/F=9.0g·h/mol, 2.1MPa, 375℃, feed: Ar/H_2/CO/CO_2=3/65/24/8,
Catalyst A no Pd, Catalyst B,C,D contains small amount of Pd

2.2. The optimization of reaction conditions over hybrid catalysts

Compared with Cu-Zn, Cr-Zn showed a lower activity for methanol synthesis from syngas. The increase in the reaction pressure would benefit the formation of methanol. As Fig.2 shows, a high reaction pressure promoted the CO conversion, yield of hydrocarbons, and selectivity for LPG. Also, the yield of methane decreased at high reaction pressure. This is favorable because methane is the most unfavorable product in this process. Therefore, the medium reaction

pressure (3.0-6.0MPa) was suitable for the LPG synthesis from syngas, because the high catalytic activity is essential for the commercial application.

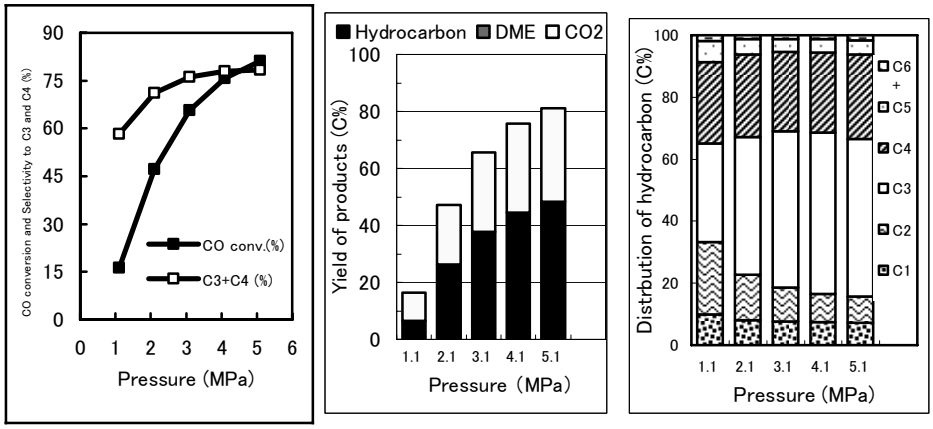

Fig. 2 Effect of reaction pressure
Reaction conditions: 400°C, 8.9 mol/(h.g catalyst), Syngas: Ar: CO: H2 = 3: 32: 65, Catalyst: 1.0g

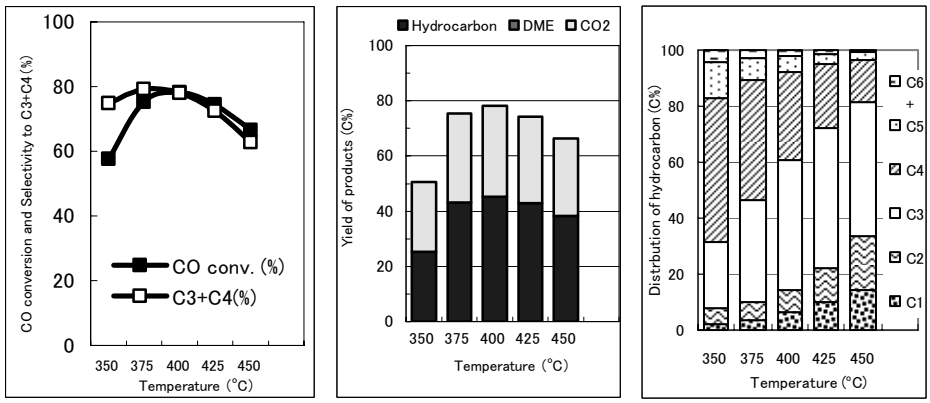

Fig. 3 Effects of reaction temperature
Reaction conditions: 5.1MPa, 8.9 mol / (h.g catalyst), Syngas: Ar:CO:H_2=3:32: 65, Catalyst: 1.0g

Fig.3 shows the CO conversion and the hydrocarbon distribution as a function of reaction temperatures. When the reaction temperature was raised, the selectivity of C_1 and C_2 hydrocarbons increased while C_4, C_5 and C_6+ hydrocarbons decreased. The CO conversion reached the maximum at 400℃ while the selectivity for LPG kept at high level. However, the high reaction temperature was not favored by equilibrium yield of methanol from syngas, and the rate of methanol formation become the rate control for hydrocarbon synthesis from synthesis gas over hybrid

catalyst. Low concentration of methanol and DME, as intermediates from synthesis gas to hydrocarbons, would restrict the rate of hydrocarbon formation. Thus high reaction temperature decreased the CO conversion. Temperature also showed a worked effect on the distribution of hydrocarbon products. At low temperature, the average molecular weight of the product hydrocarbons was larger than that at high temperature, where direct hydrogenation of CO into methane or the hydro-cracking of higher hydrocarbon catalyzed by Pd may result in the high yield of methane. Also, high temperature enhanced cracking rate of C_4-C_6+ hydrocarbons, resulting in the decrease in the heavy hydrocarbons selectivity, which was deleterious for the activity of zeolite. So the appropriate temperature of reaction is 370-400^{o}C.

The flow rate of syngas played a main role in the CO conversion and distribution of product hydrocarbons. As Fig.4 shows, the CO conversion increased with an increase of W/F as usual while keeping the total selectivity for LPG almost constant. The selectivity for light hydrocarbons (C_1, C_2 and C_3) increased while the selectivity for the heavy hydrocarbons (C_4, C_5 and C_6+) decreased when the contact time(W/F) increased, probably because of secondary reaction of C_5+ hydrocarbons. That the low W/F also resulted in a low CO conversion and low the selectivity for LPG fraction was attributed to the formation rate of methanol from synthesis gas was the rate-determining step in the total process of synthesis of hydrocarbons.

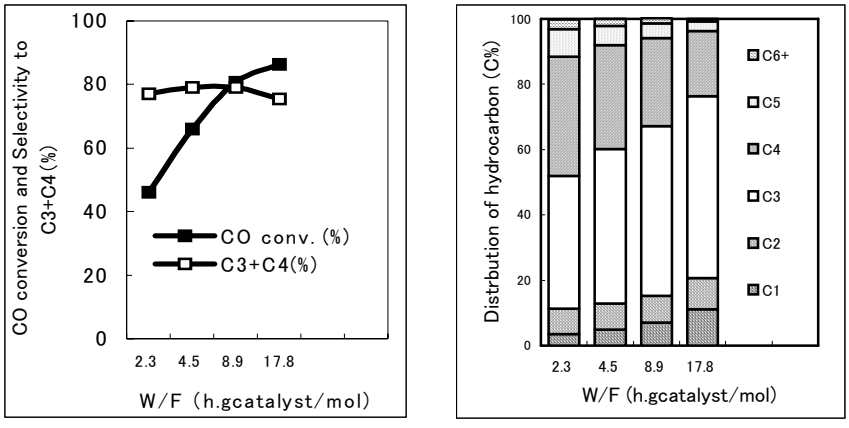

Fig.4 Effects of contact time.
Reaction conditions: 400^{o}C, 5.1MPa, Syngas: Ar: CO: H_2 = 3: 32: 65, Catalyst: 1g

2.3. The catalytic stability of hybrid catalysts

The stability experimental results (Fig. 5) exhibit that the Zn-Cr hybrid catalyst show the good catalytic stability, the CO conversion and LPG selectivity could keep >65% and 75%, respectively, during 150 hours operation. The high selectivity to LPG over low content Pd-modified hybrid catalyst was attributed

to three dimensions structure and large pore size of β-zeolite. Olefins (propylene and butenes) in product hydrocarbons formed in the cage of zeolite would easily leave the active site and diffused to the surface of palladium for hydrogenation reaction. Hydrogenation of olefins would stop the growth of carbon chain and decrease the yield of heavy hydrocarbons and coke. There was no olefin found in the product, because the intermediate olefins produced from methanol or DME were hydrogenated in situ catalyzed by Pd.

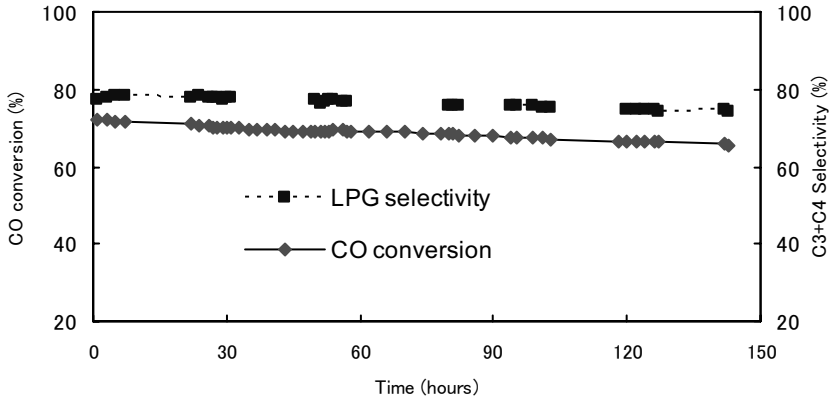

Figure 5. The stability experiments of Zn-Cr hybrid catalyst at 375°C, 5.0MPa, 9 g·h/mol.

3. Summary

The modification of Cr-Zn catalyst by Pd increased the activity and selectivity for LPG synthesis and modification of β-zeolite increased stability of the hybrid catalyst. The medium reaction pressure (3.0-5.0MPa) was suitable for LPG synthesis from syngas using the hybrid catalyst giving 78% CO conversion and 79% LPG and 15% light naphtha selectivity. Based on these results, a bench scale plant whose capacity is 1Kg/day is now under operation.

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